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(54) Fluorine-containing copolymer having rings on its main chain

(57) A fluorine-containing copolymer comprising (a) polymer units based on a fluoroolefin, (b) polymer units based on a cyclic monomer having, on its ring, an unsaturated group copolymerizable with the fluoroolefin, (c) polymer units based on an ethylenically unsaturated compound having a curable moiety but having neither an ester bond nor an ether bond, and optionally (d) polymer units based on at least one olefin selected from ethylene, propylene and isobutylene, or polymer units based on a vinyl ether having an aliphatic ring, in such proportions that, based on the total amount of polymer units (a), (b), (c) and (d), polymer units (a) are from 35 to 65 mol%, polymer units (b) are from 5 to 45 mol%, polymer units (c) are from 1 to 30 mol% and polymer units (d) are from 0 to 40 mol%, which has a number average molecular weight within a range of from 2,000 to 100,000, as calculated as polystyrene by gel permeation chromatograph, and which has rings based on said cyclic monomer, on the main chain of the copolymer.

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based on said cyclic monomer, on the main chain of the copolymer.

Further, the present invention provides a resin composition for coating, which comprises such a fluorine-containing copolymer and a curing agent, and a resin composition for powder coating comprising such a fluorine-containing copolymer and a curing agent.

Now, the present invention will be described in detail with reference to the preferred embodiments.

The fluoroolefin which gives polymer units (a), is a polymerizable olefin having at least one fluorine atom. Specifically, tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, vinylidene fluoride, pentafluoropropylene or hexafluoropropylene is preferred. Particularly preferred is a C_{2-3} perhaloolefin such as tetrafluoroethylene, chlorotrifluoroethylene or hexafluoropropylene.

When the stability during polymerization, storage stability and low coloring are important, a fluoroolefin containing no chlorine atom is preferred. Particularly preferred is tetrafluoroethylene from the viewpoint of the stability during polymerization.

Polymer units (b) are polymer units based on a cyclic monomer having, on its ring, an unsaturated group copolymerizable with the fluoroolefin, and the copolymer of the present invention has rings derived from this cyclic monomer on its main chain. The copolymer having rings on its main chain means that at least two carbon atoms constituting each ring are carbon atoms in the carbon chain constituting the main chain of the copolymer.

The monomer which gives polymer units (b), is not particularly limited so long as it is a monomer having a cyclic unsaturated group copolymerizable with the fluoroolefin. A compound is preferred in which such a ring is an aliphatic ring or a heterocyclic ring. Further, this monomer is preferably one having no ester bond.

The compound wherein the above ring is an aliphatic ring, may, for example, be a compound having at least two aliphatic rings, such as a norbornadiene, a norbornene or a dicyclopentadiene, or a compound having one aliphatic ring, such as cyclohexene, cyclopentene or cyclopentadiene.

The norbornadiene may, for example, be a 2,5-norbornadiene having an aryl group, such as 2-acetoxy-3-phenyl-2,5-norbornadiene, or 2,5-norbornadiene.

The norbornene may, for example, be a 2-norbornene having an alkyl group, such as 5-ethylbicyclo[2.2.1]hepto-2-ene, a 2-norbornene having an alkalidene group, such as 5-ethylidene bicyclo[2.2.1]hepto-2-ene, a 2-norbornene having a alkenyl group, such as 5-vinylbicyclo[2.2.1]hepto-2-ene or 5-allylbicyclo[2.2.1]hepto-2-ene, a 2-norbornene having an aryl group, such as 3-phenyl-2-norbornene, or 2-norbornene.

When the monomer which gives polymer units (b), has an alkenyl group, the alkenyl group has low polymerizability as compared with the unsaturated group in the ring, and the alkenyl group will remain after polymerization. Such an alkenyl group may be oxidized to convert it to an epoxy group, or may be utilized as it is, as a vulcanizable moiety.

As a compound wherein the above ring is a heterocyclic ring, dihydrofuran, furan, γ-pyran, pyrrole or thiophene may, for example, be mentioned.

From the viewpoint of giving polymerizability and high Tg, 5-ethylidene bicyclo[2.2.1]hepto-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, 2,5-norbornadiene or 2-norbornene is preferred. Particularly preferred is 2,5-norbornadiene or 2-norbornene.

Polymer units (c) are polymer units based on an ethylenically unsaturated compound having a curable moiety but having neither an ester bond nor an ether bond. The monomer for polymer units (c) is a monomer having no ring or a monomer having a ring provided that the ring has no unsaturated group copolymerizable with the fluoroolefin, and thus is different from the monomer for polymer units (b).

The curable moiety may, for example, be a hydroxyl group, an epoxy group, a carboxyl group, a carboxylic anhydride group, a hydrolyzable silyl group, an amino group, a carbonyl group, a thiol group or an aldehyde group. When the fluorine-containing copolymer of the present invention is applied to a powder coating material, the curable moiety is particularly preferably a hydroxyl groups, an epoxy group or a carboxyl group.

It is essential that polymer units (c) contain neither an ester bond nor an ether bond, and it is preferred that they have no fluorine atom. From the viewpoint of the polymerization yield, storage stability, availability, reactivity with a curing agent and boiling point, the monomer having a hydroxyl group is preferably an α-olefin having a hydroxyl group, the monomer having an epoxy group is preferably an epoxy compound having a vinyl group, and the monomer having a carboxyl group is preferably an unsaturated carboxylic acid.

The α-olefin having a hydroxyl group is preferably allyl alcohol. The epoxy group having a vinyl group may, for example, be an alicyclic epoxy compound having a vinyl group, such as 3-vinylcyclohexene oxide, or a linear or branched epoxy compound, such as 1,3-butadiene monoepoxide.

The unsaturated carboxylic acid may, for example, be 3-butenoic acid, 4-pentenoic acid, 3-hexenoic acid, 4-hexenoic acid, 5-hexenoic acid, 5-heptenoic acid, 6-heptenoic acid, 6-octenoic acid, 7-octenoic acid, 7-nonenoic acid, 8-nonenoic acid, 8-decenoic acid, 9-decenoic acid, 9-undecenoic acid, 10-undecenoic acid, 11-tridecenoic acid or 12-tridecenoic acid. Further, a monomer having a carboxyl group blocked by a vinyl ether may be copolymerized and then dissociated under an acidic condition.

The monomer which gives polymer units (d) is an optional component, and the copolymer may not contain polymer

The dibasic acid having carboxyl groups blocked, may be a hydrazide compound such as adipic acid dihydrazide, sebacic acid dihydrazide, dodecanedioic acid dihydrazide, eicosanedioic acid dihydrazide, isophthalic acid dihydrazide, azelaic acid dihydrazide, suberic acid dihydrazide or pyromellitic acid tetrahydrazide.

Further, a compound having the above dibasic acid blocked with a vinyl ether may also be used. Here, the vinyl ether may, for example, be an alkylvinyl ether such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, sec-butyl vinyl ether or tert-butyl vinyl ether.

When the above curing agent is used, a curing assisting catalyst may be used in combination to accelerate the curing reaction. Such a curing assisting catalyst may, for example, be an imidazole or its derivative, or an amine compound such as diaminodiphenylmethane or 1,8-diazabicyclo[5.4.0]undeca-7-ene . Further, in order to improve the storage stability at room temperature, an organic acid such as formic acid or acetic acid may be used in combination.

The polycarboxylic anhydride may, for example, be succinic anhydride, phthalic anhydride, hexahydrophthalic anhydride, 4-methylhexahydrophthalic anhydride, trimellitic anhydride or pyromellitic anhydride or polyacid anhydride (ADDITOL VXL1381: tradename, manufactured by Vianova Co.). Further, when the fluorine-containing copolymer has epoxy groups, curing may be carried out by means of a cationic polymerization catalyst. When heated, this catalyst is activated to produce cation species or a Lewis acid, whereby ring opening polymerization of epoxy groups will be carried out. As such a catalyst, an aromatic sulfonyl salt may, for example, be mentioned. Further, a copper complex of imidazole as disclosed in Polymer Bulletin 33, 347-353, 1994, may similarly be used.

When the curable moieties of the fluorine-containing copolymer are hydroxyl groups only, it is preferred to use a blocked isocyanate compound, an urethodione compound or a tetramethoxyglycoluryl (POWDERLINK 1174: tradename, manufactured by American Cyanamid Co., Ltd.) as a curing agent.

The blocked isocyanate compound may, for example, be a polyisocyanate compound such as hexamethylene diisocyanate, isophorone diisocyanate, tolylene diisocyanate or xylylene diisocyanate having isocyanate groups blocked with a blocking agent such as ε-caprolactam, phenol or methyl ethyl oxime ketone, or a polyisocyanate compound, such as a dimer or trimer of such a polyisocyanate compound. Further, a curing assisting catalyst such as dibutyltin dilaurate may be used in combination.

When the fluorine-containing copolymer has carboxyl groups as the curable moieties, a compound having an epoxy group, or a compound having an acid amide group, may be used as the curing agent. Specifically, triglycidyl isocyanurate or polyepoxide may, for example, be mentioned.

In a case where the fluorine-containing copolymer of the present invention is used as a resin composition for coating, if a polymer having hydrophilic groups, is incorporated, it is possible to impart a hydrophilic nature to the coating film, whereby rain streak fouling resistance can be improved. Here, the polymer having hydrophilic groups is preferably a partial hydrolyzate of polyvinyl acetate, a partial hydrolyzate of an ethylene-vinyl acetate copolymer, or an acrylate or methacrylate polymer having an addition polymer of ethylene oxide in its side chain.

The polymer having hydrophilic groups, preferably has a Mn of from 500 to 5,000, more preferably from 500 to 2000, whereby it scarcely falls off from the coating film surface, and the fluidity during coating will be good.

The above-mentioned partial hydrolyzate is preferably a partial hydrolyzate having a hydrolysis ratio of from 70 to 90%, whereby an adequate hydrophilic nature can be obtained, and the hygroscopic nature is not so high that when it is used for powder coating, the powder is scarcely susceptible to blocking.

In the acrylate or methacrylate polymer having an addition polymer of ethylene oxide on its side chain, the polymerization degree of ethylene oxide is preferably from 5 to 20. This polymer may be one having an acrylate or methacrylate having a fluoroalkyl group copolymerized.

When the polymer having hydrophilic groups is incorporated to the resin composition for coating of the present invention, the blend proportion is preferably from 1 to 20 parts by weight, more preferably from 1 to 10 parts by weight, per 100 parts by weight of the fluorine-containing copolymer. By such a blend proportion, a proper hydrophilic nature is obtainable and rain streak fouling is less likely to result, and when it is used for powder coating, the hygroscopic nature of the powder will not be so high that blocking of the powder is less likely.

When the curable moieties of the fluorine-containing copolymer are epoxy groups, the epoxy equivalent is preferably within a range of from 250 to 3,000 mgKOH/g, more preferably from 600 to 1,500 mgKOH/g. If the epoxy equivalent is too small, the coating film tends to be hard and brittle, and if it is too large, the mechanical strength of the coating film tends to be poor.

When the curable moieties of the fluorine-containing copolymer are hydroxyl groups, the hydroxyl value is preferably within a range of from 10 to 150 mgKOH/g. When the curable moieties of the fluorine-containing copolymer are carboxyl groups, the acid value is preferably within a range of from 10 to 200 mgKOH/g. If the hydroxyl value or the acid value is too small, the mechanical strength of the coating film tends to be poor, and if the hydroxyl value or the acid value is too large, the coating film tends to be hard and brittle.

When the fluorine-containing copolymer has epoxy groups and hydroxyl groups, the hydroxyl value is preferably from 10 to 100 mgKOH/g, and the epoxy equivalent is preferably within a range of from 600 to 3,000 mgKOH/g.

When the fluorine-containing copolymer of the present invention is used for powder coating, the above-mentioned

Table 2 (continued)

Veova-9	Tradename for an vinyl ester of a branched carboxylic acid (carbon number: 9) manufactured by Shell Co.
HCFC225	Dichloropentafluoropropane
PBPV	t-Butyl peroxypivalate
TGI	Triglycidyl isocyanurate
DBTDL	Dibutyltin dilaurate

EXAMPLE 1

Into a stainless steel autoclave having an internal capacity of 2.5 ℓ and equipped with a stirrer (pressure resistance: 50 kg/cm^{2}G), 40.3 g of NBD, 27.5 g of CHVE and 12.7 g of AA were charged, and dissolved air was removed by repeating deaeration under cooling and pressurizing by nitrogen gas.

Then, 1,777 g of HCFE225 and 131.3 g of TFE were introduced into the autoclave, and the temperature was raised.

When the temperature in the autoclave reached 60°C, the pressure became 10.0 kg/cm^{2}G. Then, 2 cc of a 50% HCFC225 solution of PBPV was added, and the reaction was initiated. While maintaining the pressure as the pressure decreased, 218.8 g of TFE, 70.0 g of CHVE, 100.8 g of NBD and 31.7 g of AA were continuously added to carry out the reaction continuously.

During the reaction, 23 cc of a 50% HCFC225 solution of PBPV was continuously added. Ten hours later, feeding the respective monomers was stopped, and the reaction was continued to 2 kg/cm^{2}G. Then, the autoclave was cooled with water to terminate the reaction.

When the temperature reached room temperature, unreacted monomers were purged, and the autoclave was opened. The obtained polymer was dried under reduced pressure of 4 mmHg over 5 hours to remove the solvent and then pulverized by an impact hammer mill to obtain a powder of a fluorine-containing copolymer. The results of the analysis of the composition by ^{13}C-NMR are shown in the upper portion in Table 3 (at the righthand side of "/"). Further, the composition of charged monomers is shown in the upper portion in Table 3 (at the lefthand side of "/").

EXAMPLES 2 to 17

In the same manner as in Example 1, copolymerization was carried out with the compositions of charged monomers as identified in the upper portions in Tables 3 to 5 (the lefthand side of "/") to obtain powders of fluorine-containing copolymers. The results of the analyses of the compositions by ^{13}C-NMR are likewise shown in the upper portions in Tables 3 to 5 (the lefthand side of "/").

Symbols a to d in the column of the monomers in Tables 3 to 5 indicate the types of the monomers corresponding to polymer units (a) to (d).

Measurement of the physical properties

Mn, Tg and the thermal stability (increase in the molecular weight after heating at 120°C for 5 hours: ◎ indicates an increase of less than 1.1, ○ less than 1.2, △ less than 1.4, and X at least 1.4) of the fluorine-containing copolymers obtained in Examples 1 to 17 are shown in the lower portions in Tables 3 to 5.

EXAMPLE 18

Into a three-necked separable flask having an internal capacity of 1 ℓ, 23.2 g of methyl methacrylate, 8.7 g of NK ester M-40G (tradename for polyethylene glycol monomethacryl ester, manufactured by Shin Nakamura Kagaku K.K., polymerization degree of ethylene oxide: 7), 26.2 g of styrene and 300 g of butyl acetate, were charged, and the upper spatial portion was flushed with nitrogen gas. The temperature was raised to 80°C, and then 0.8 g of azobisisobutyronitrile was added to initiate the reaction. Then, as the polymerization proceeded, 70 g of methyl methacrylate, 26.2 g of NK ester M-40G and 78.5 g of styrene were added to let the reaction proceed.

Six hours later, the reaction was terminated, and after cooling, the obtained polymer was dried under a reduced pressure of 4 mmHg for 5 hours to remove the solvent, and then pulverized by an impact hammer mill, to obtain a powder of a hydrophilic copolymer (Mn: about 2,000) composed of an acrylic copolymer having hydrophilic groups.

Table 4

Monomer (mol%)		Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
a	TFE	60/49					50/48
a	CTFE		60/52	50/51	50/51	50/50	
b	NBD	20/21	20/25				
c	VCHO	10/16					
d	CHVE	10/14		20/19			
	VP		10/15	20/22	20/21		20/22
	Veova-9				20/20	20/22	10/9
	VB					10/8	10/9
	HBVE			10/8			10/12
	HEAE				10/8	10/9	
	HEC		10/8				
	AGE					10/11	
Mn		8,100	5,300	8,100	5,40	4,600	6,700
Tg (°C)		72	62	58	52	49	43
Thermal stability		◎	X	X	X	X	X

Table 5

Monomer (mol%)		Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17
a	TFE		60/51	60/52		
a	HFP	70/42				
a	TriFE					
a	CTFE				50/51	50/50
b	NBD	15/23		15/22		
b	NB		20/23			
c	UA				10/8	
c	AA	5/13				
d	ET	10/22		10/15		
d	IBT		10/15			
	VP				20/21	10/8
	Veova-9				20/20	20/22
	HEAE		5/6			
	AGE		5/5	15/11		10/9
	HBVE					10/11
Mn		4,300	7,300	5,100	5,400	4,600
Tg (°C)		46	51	43	52	49

Table 7

	Ex. 24	Ex. 25	Ex. 26	Ex. 27
Fluorine-containing copolymer				
Example 6	37			
Example 7		38		
Example 8			37	
Example 9				36
Hydrophilic copolymer				
MERCENE H-6960	3.7			
MERCENE H-6822X		3.8		
VINYL ALCOHOL #500			3	
VINYL ALCOHOL #2000				3.6
Curing agent				
ADDUCT B-1530			5.3	
CORONATE 2507	8.8			4.7
Dodecanedioic acid				
Dodecanedioic acid dihydrazide		12.8		
Catalyst				
2-Methylimidazole		0.2		
DBTDL	0.12		0.12	0.12
Additives				
MODAFLOW 2000	0.5	0.5	0.5	0.5
TINUVIN 900	2	2	2	2
TINUVIN 144	0.7	0.7	0.7	0.7

Table 10

	Ex.19	Ex.20	Ex.21	Ex.22	Ex.23	Ex.24	Ex.25
Storage stability of the coating material	Good	Good	Good	Good	Good	Good	Good
Solvent resistance	Good	Good	Good	Good	Good	Good	Good
Acid resistance	O	O	O	O	O	O	O
Fouling resistance	O	O	O	O	O	O	O
Weather resistance	98	97	99	95	98	99	98

Table 11

	Ex.26	Ex.27	Ex.28	Ex.29	Ex.30
Storage stability of the coating material	Bad	Bad	Bad	Good	Bad
Solvent resistance	Good	Good	Good	Good	Good
Acid resistance	O	O	△	O	O
Fouling resistance	O	O	O	△	△
Weather resistance	99	97	92	96	88

The fluorine-containing copolymer of the present invention gives a coating film excellent in chemical resistance, antifouling properties, weather resistance, etc., and presents excellent storage stability or efficiency for drying for e.g. a powder coating material. By using such a fluorine-containing copolymer and a polymer having hydrophilic groups in combination, it is possible to obtain a coating film excellent in rain streak fouling resistance.

Claims

1. A fluorine-containing copolymer comprising (a) polymer units based on a fluoroolefin, (b) polymer units based on a cyclic monomer having, on its ring, an unsaturated group copolymerizable with the fluoroolefin, (c) polymer units based on an ethylenically unsaturated compound having a curable moiety but having neither an ester bond nor an ether bond, and optionally (d) polymer units based on at least one olefin selected from ethylene, propylene and isobutylene, or polymer units based on a vinyl ether having an aliphatic ring, in such proportions that, based on the total amount of polymer units (a), (b), (c) and (d), polymer units (a) are from 35 to 65 mol%, polymer units (b) are from 5 to 45 mol%, polymer units (c) are from 1 to 30 mol% and polymer units (d) are from 0 to 40 mol%, which has a number average molecular weight within a range of from 2,000 to 100,000, as calculated as polystyrene by gel permeation chromatograph, and which has rings based on said cyclic monomer, on the main chain of the copolymer.

2. The fluorine-containing copolymer according to Claim 1, wherein the ring of the cyclic monomer is an aliphatic ring or a heterocyclic ring.

3. The fluorine-containing copolymer according to Claim 1 or 2, wherein the cyclic monomer is a norbornadiene or a norbornene.

4. The fluorine-containing copolymer according to Claim 1, 2 or 3, wherein the curable moiety of polymer units (c) is an epoxy group, a hydroxyl group or a carboxyl group.

5. The fluorine-containing copolymer according to any one of Claims 1 to 4, wherein polymer units (c) are polymer units based on an allyl alcohol, an epoxy compound having a vinyl group, or an unsaturated carboxylic acid.

6. A resin composition for coating, which comprises the fluorine-containing copolymer as defined in anyone of claims

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EUROPEAN SEARCH REPORT

Application Number
EP 97 12 0995

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 283 304 A (NAKABAYASHI AKIRA ET AL) 1 February 1994 * column 6, line 50 - column 11, line 20; claims 1-22 *	1,2,4-8	C08F214/18 C08F232/02 C09D127/12
X	EP 0 372 805 A (MITSUI PETROCHEMICAL IND) 13 June 1990 * page 3, line 49 - page 5, line 36 * * page 10, line 14-30 *	1,2,4-8	
X	EP 0 437 619 A (DAIKIN IND LTD) 24 July 1991 * abstract * * page 2, line 27 - page 7, line 29; claims 1-13 *	1-8	
X	US 4 701 508 A (HOMMA SHIROU ET AL) 20 October 1987 * column 2, line 45 - column 5, line 44 *	1,2,4-8	
X Y	EP 0 464 704 A (DAIKIN IND LTD) * page 2, line 27 - page 5, line 47 * * page 8, line 11 - page 9, line 50 *	1,2,4-8 3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08F C09D
X	EP 0 312 834 A (ASAHI GLASS CO LTD) 26 April 1989 * page 2, line 51 * * page 2, line 25 - page 4, line 14; claims 1-8 *	1,2,4-8	
Y	PATENT ABSTRACTS OF JAPAN vol. 018, no. 415 (C-1233), 4 August 1994 & JP 06 122730 A (TOAGOSEI CHEM IND CO LTD), 6 May 1994, * abstract *	3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 March 1998	Hammond, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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